Supporting information

Targeted design of heterotrimetallic 1-D coordination polymers based on functionalized metallocenes featuring an antibacterial activity

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Experimental

IR spectra were recorded in the 400–4000 cm^{-1} region using a Spectrum-65 Perkin Elmer FT-IR spectrometer taken from polycrystalline samples. Microprobe analyses were carried out using a Carlo Erba EA 1108 Series CHN Elemental Analyzer.

For the analysis on metals we used a mass spectrometric method with inductively coupled plasma (ICP-MS) (Agilent 7500ce; Agilent Technologies Inc., USA).

Crystallography

Single crystal X-ray diffraction experiment for **1**–**4** were performed with a Bruker APEX2 diffractometer with graphite monochromated Mo-Kα radiation (lλ = 0.71073 Å)[1]. A semiempirical adsorption correction has applied using the SADABS program [2] and refined in a full-matrix OLS using the Olex2 program [3], the structures were solved with the ShelXT [4] structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least-Squares minimization against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of OH groups and those of water molecules were located from difference Fourier synthesis, positions of other hydrogen atoms were calculated, and they all were refined in isotropic approximation within the riding model.

Crystal data and refinement parameters for **1**–**4** are given in Tables S1. The structural data of compounds **1–4** are deposited in the Cambridge Structural Data Bank (CCDC № (CCDC № 2330528 (**1**), 2330529 (**2**), 2330530 (**3**), 2330531 (**4**) deposit@ccdc.cam.ac.uk.deposit@ccdc.cam.ac.uk.

Table S1. Crystallographic parameters and details of structures refinement of **1**-**4**.

Parameter	Value			
	1	**2**	**3**	**4**
M, g/mol	989.76	1359.35	1562.85	1560.27
T, K	296	296	150(2)	150(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.130(4)	11.799(3)	11.261(4)	11.2271(11)
b, Å	11.153(2)	12.068(3)	12.185(5)	12.1730(12)
c, Å	12.193(2)	12.269(3)	12.516(5)	12.4586(12)
α, deg	117.157(2)	69.334(3)	68.836(6)	68.883(2)
β, deg	97.065(3)	78.013(4)	78.965(7)	78.970(2)
γ, deg	102.710(4)	65.678(4)	70.326(6)	70.241(2)
V, Å^3	1155.4(6)	1485.5(6)	1503.2(10)	1490.1(3)
Z	1	1	1	1
ρ(calc.), g cm^{-3}	1.422	1.520	1.726	1.739
μ, mm^{-3}	1.350	1.881	1.798	1.738
θ_{min}–θ_{max}, deg	1.943– 30.000	2.205– 24.711	2.261– 29.995	2.121– 29.998
F(000)	518	678	787	782
T_{min}/T_{max}	0.878/0.898	0.910/0.963	0.598/0.657	0.652/ 0.698
Total reflections	13613	9510	14252	17655
Independent reflections	6675	5010	8268	8611
R_{int}	0.0185	0.1002	0.0660	0.0428
Reflections with $I > 2\sigma(I)$	5616	2048	4245	5596
GOOF	1.040	0.959	0.960	1.014
R-factors $F^2 > 2\sigma(F^2)$	$R_1 = 0.0296$; $wR_2 = 0.0379$	$R_1 = 0.0987$; $wR_2 = 0.2138$	$R_1 = 0.0687$; $wR_2 = 0.1456$	$R_1 = 0.0520$; $wR_2 = 0.0942$
R- factors for all reflections	$R_1 = 0.0755$; $wR_2 = 0.0796$	$R_1 = 0.2536$; $wR_2 = 0.3344$	$R_1 = 0.1427$; $wR_2 = 0.1771$	$R_1 = 0.1113$; $wR_2 = 0.1299$
$\Delta\rho_{min}/\Delta\rho_{max}$, *e*/Å^3	0.547/-0.368	-0.971 / 1.097	-0.753/1.025	-0.800/0.819

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Main bond lengths and interatomic distances in the structures of complexes **1-4.**

Bond	Length, Å			
	1 M = Cu	**2** M = Cu	**3** M = Ni	**4** M = Co
M–O(RCOO)	1.956(2)-1.964(2)	1.948(9)-1.978(10)	1.979(4)-1.991(4)	1.996(2)-2.006(2)
M–O (O=P)	2.126(1)	2.092(9)	2.118(5)	2.075(2)
M…M	2.608(1)	2.649(3)	2.673(2)	2.728(1)

Table S3. C-H···O interactions in the crystal packing of complexes **2-4**.

Interactions	Distance, Å				C – H···A, º
	C–H	Symmetry code	H···A	C···A	
Complex **2**					
C(4)–H(4)···O(3)	0.98	-x,2-y,1-z	2.51	3.49(2)	178
C(6)–H(6A)···O(11)	0.97	1+x,y,z	2.49	3.43(6)	163
C(7)–H(7A)···O(8)	0.95		2.47	3.24(6)	138
C(8)–H(8A)···O(5)	0.97		2.59	2.92(3)	100
C(22)–H(22)···O(12)	0.98	-x,2-y,-z	2.48	3.15(4)	126
C(23)–H(23)···O(10)	0.98	-x,1-y,-z	2.33	2.98(3)	123
Complex **3**					
C(3)–H(3)···O(11)	1.00	-x,1-y,-z	2.56	3.420(8)	145
C(4)–H(4)···O(10)	1.00	-x,-y,1-z	2.44	3.183(8)	130
C(22)–H(22A)···O(11)	0.98	-x,1-y,-z	2.57	3.356(11)	137
C(26)–H(26)···O(4)	0.98	-x,1-y,-z	2.55	3.412(14)	150
Complex **4**					
C(3)–H(3)···O(11)	1.00	-x,1-y,-z	2.56	3.426(5)	145
C(4)–H(4)···O(10)	1.00	-x,-y,1-z	2.45	3.177(5)	129
C(19)–H(19A)···O(2)	0.99		2.58	3.440(6)	145
C(22)–H(22A)···O(11)	0.98	-x,1-y,-z	2.60	3.371(7)	136
C(26)–H(26)···O(4)	0.96	1-x,-y,1-z	2.57	3.425(8)	150

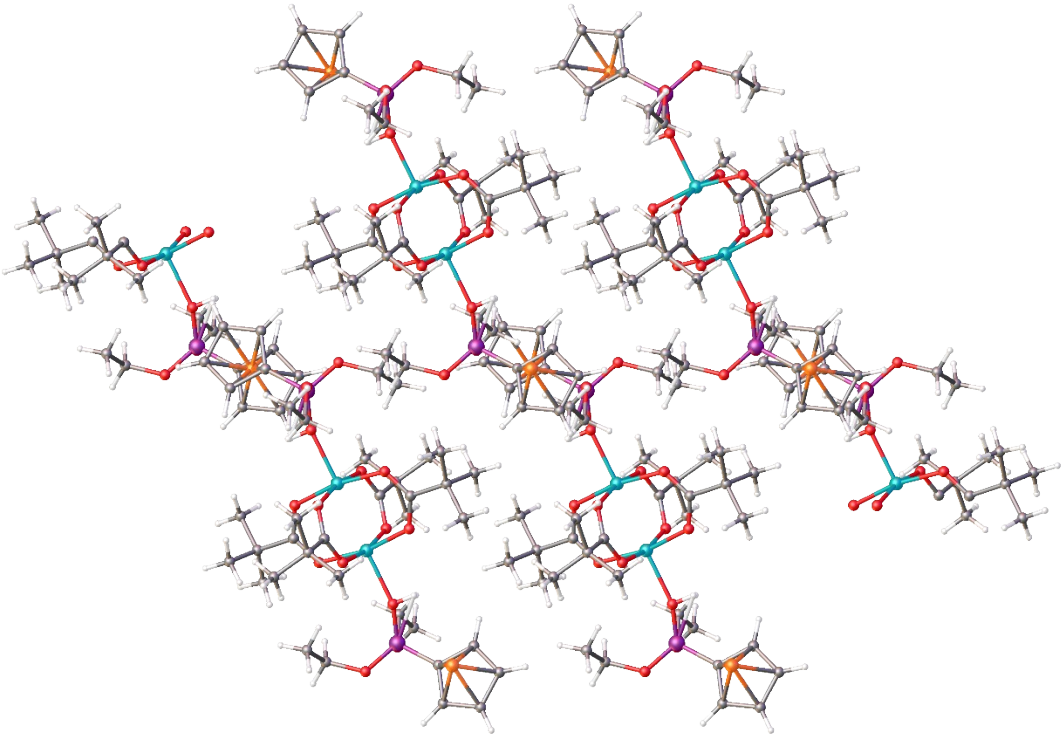

Figure S1. Crystal packing of **1.**

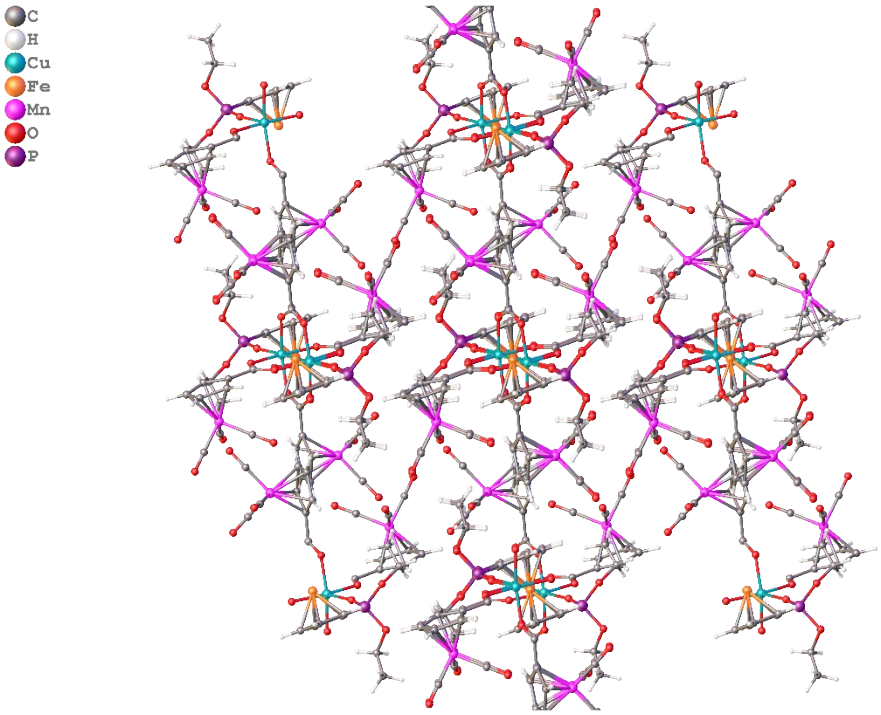

Figure S2. Crystal packing of **2.**

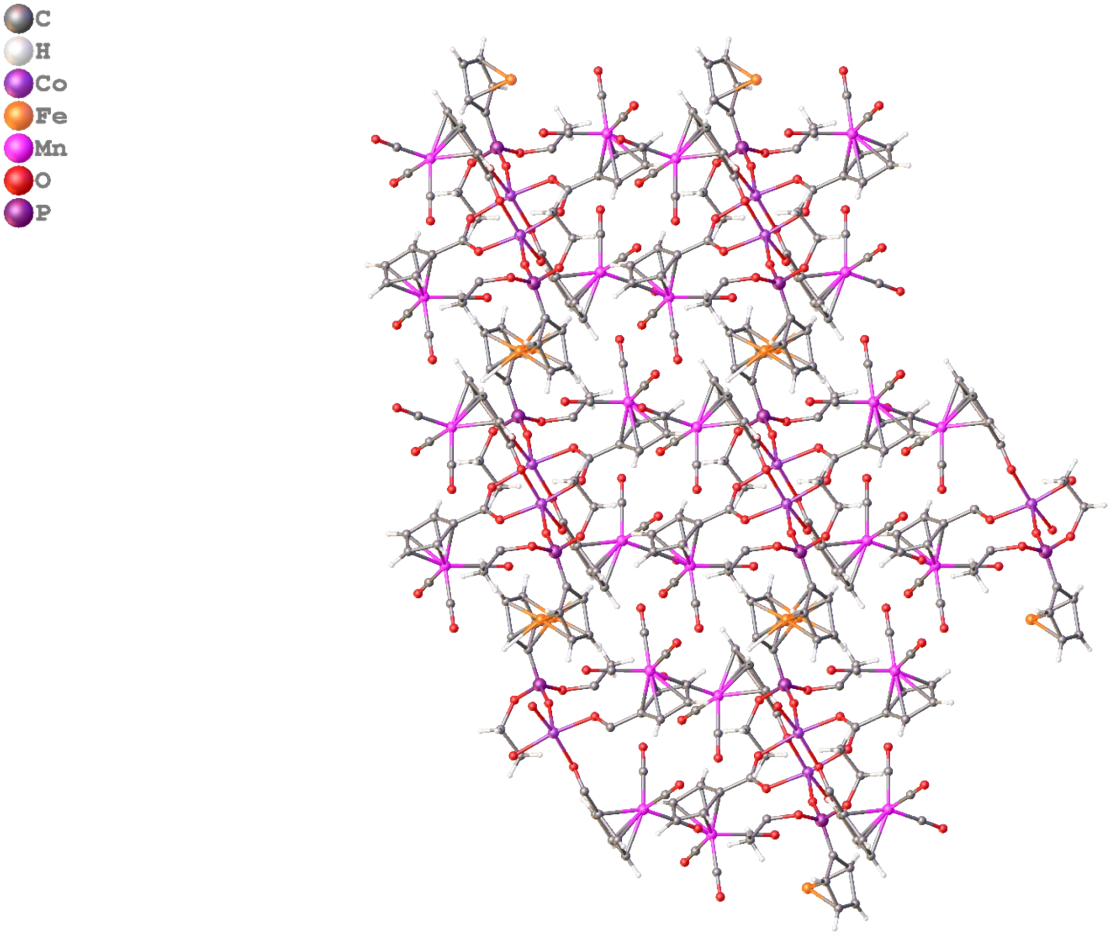

Figure S3. Crystal packing of 3,4.

Thermal behavior

The thermal behavior of complexes was studied using the simultaneous thermal analysis (STA) technique for parallel recording of TG (thermogravimetry) and DSC (differential scanning calorimetry) curves. The study was performed on an STA 449 F1 Jupiter instrument («NETZSCH») in Al-crucibles under a lid with a hole to ensure a vapor pressure of 1 atm during the thermal decomposition of the samples. The rate of heating to 900 °C was 10 °C min^{-1} under an argon atmosphere (content Ar > 99.998%, O_2 < 0.0002%, N_2 < 0.001%, water vapor < 0.0003%, CH_4 < 0.0001%).

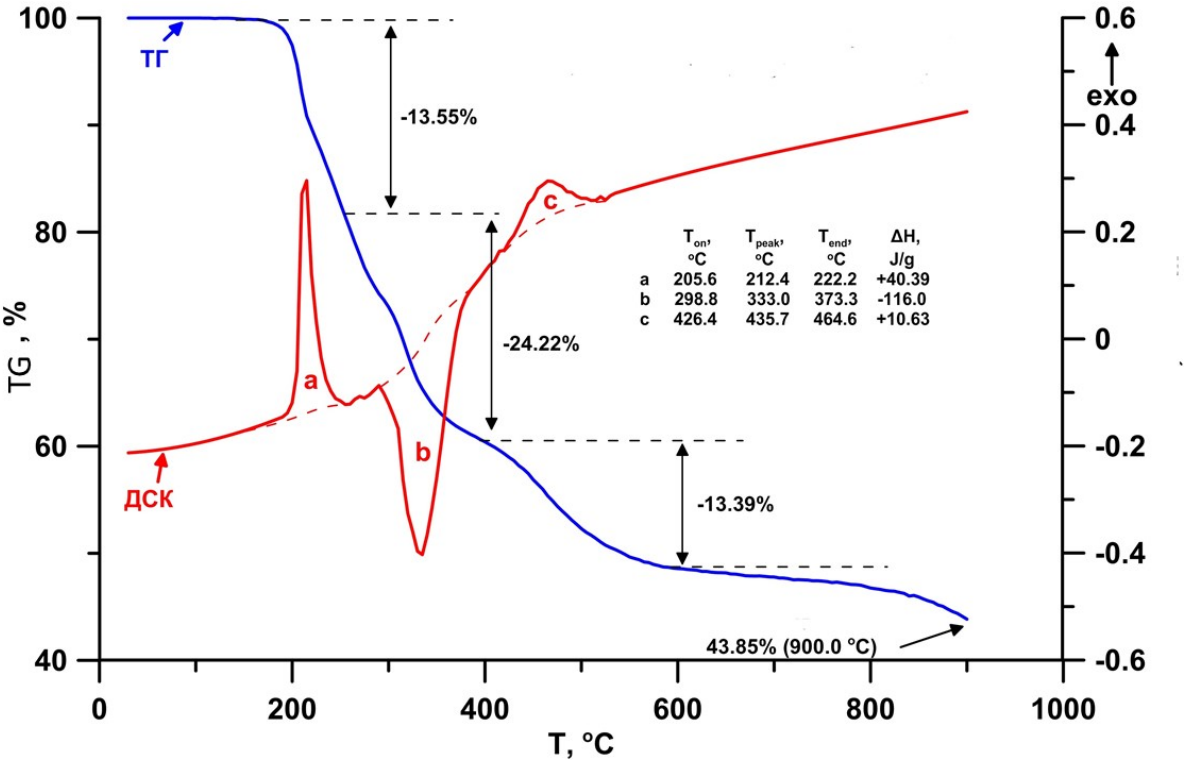

Figure S4. TG (blue) and DSC (red) curves of complexes **2.**

Antibacterial activity

To determine the biological activity of substances in M. *smegmatis,* mc^2 155 test system, the paper disk method was used. The technique involved measuring the size of the inhibition zone of the growth of the strain seeded as a lawn on an agar medium, around paper disks containing the compound in various concentrations. The studied solutions were prepared by dissolving the corresponding complexes in 100 µl of dimethyl sulfoxide. Further, the obtained solutions were diluted in concentrations of 50-6.125 mM. The bacteria washed off Petri dishes with tryp- tone soya agar M-290 medium (Himedia) were grown overnight in Lemco-TW liquid medium (Lab Lemco' Powder 5 g L^{-1} (Oxoid), peptone special 5 g L^{-1} (Oxoid), NaCl 5 g L^{-1}, Tween-80) at +37 °C until the average logarithmic growth phase at optical density OD600 ¼ 1.5, then mixed with molten agar medium M-290 in a ratio of 1 : 9 : 10 (culture : Lemco-TW : M- 290) and the resulting mixture was poured as a top layer onto Petri dishes, 5 ml per dish, with 20 ml already solidified

M-290 agar medium. After the agar in the upper layer had solidified, paper discs soaked in a solution of the test substance in different were placed on the surface of the cup. The culture was incubated for 24 hours at a temperature of +37°C. The diameter of the M. smegmatis mc2 155 growth inhibition zone around a paper disk impregnated with the compound was determined. MIC (minimum inhibitory concentration) was taken as the concentration of the compound at which the growth inhibition zone was the smallest.

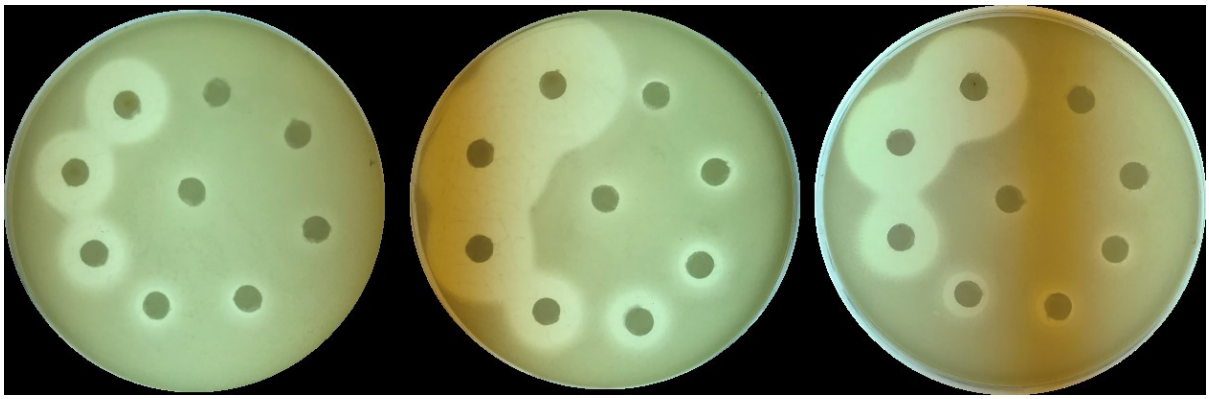

Figure S5. Photos of Petri dishes with *M.smegmatis* for **1, 2** and [Fc(O=P(OEt)$_2$)$_2$)] at different concentrations

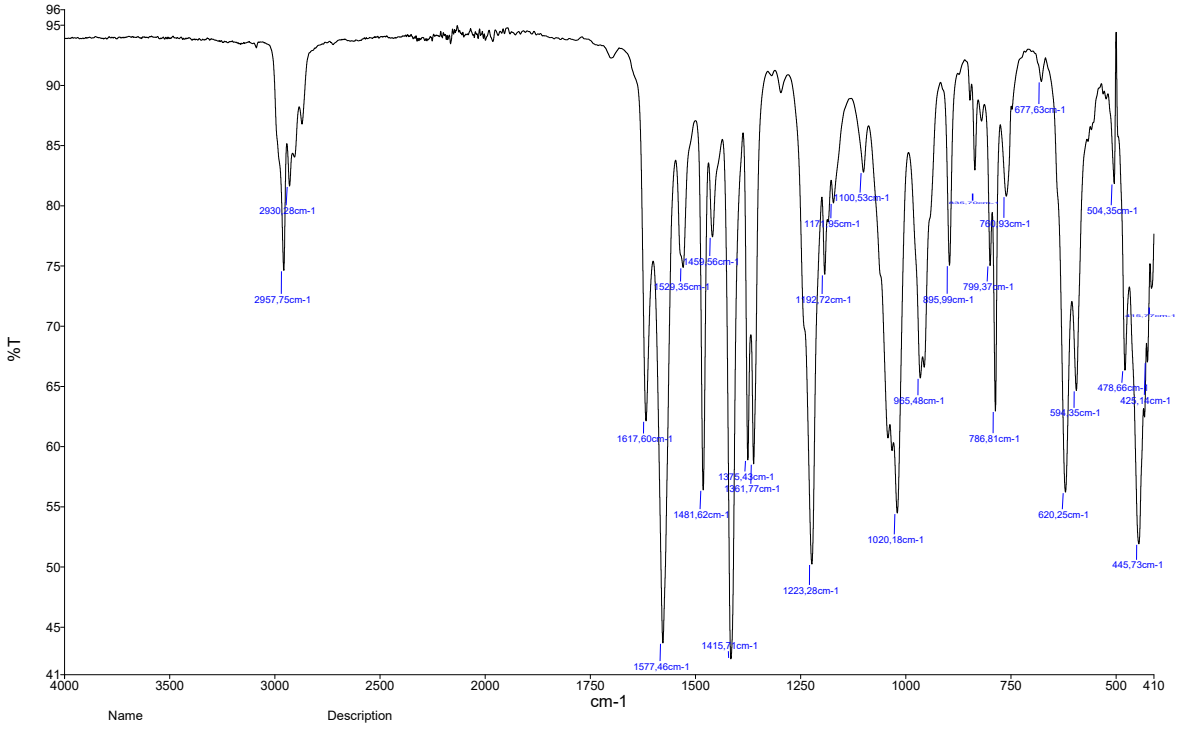

Figure S6. IR spectra of **1**.

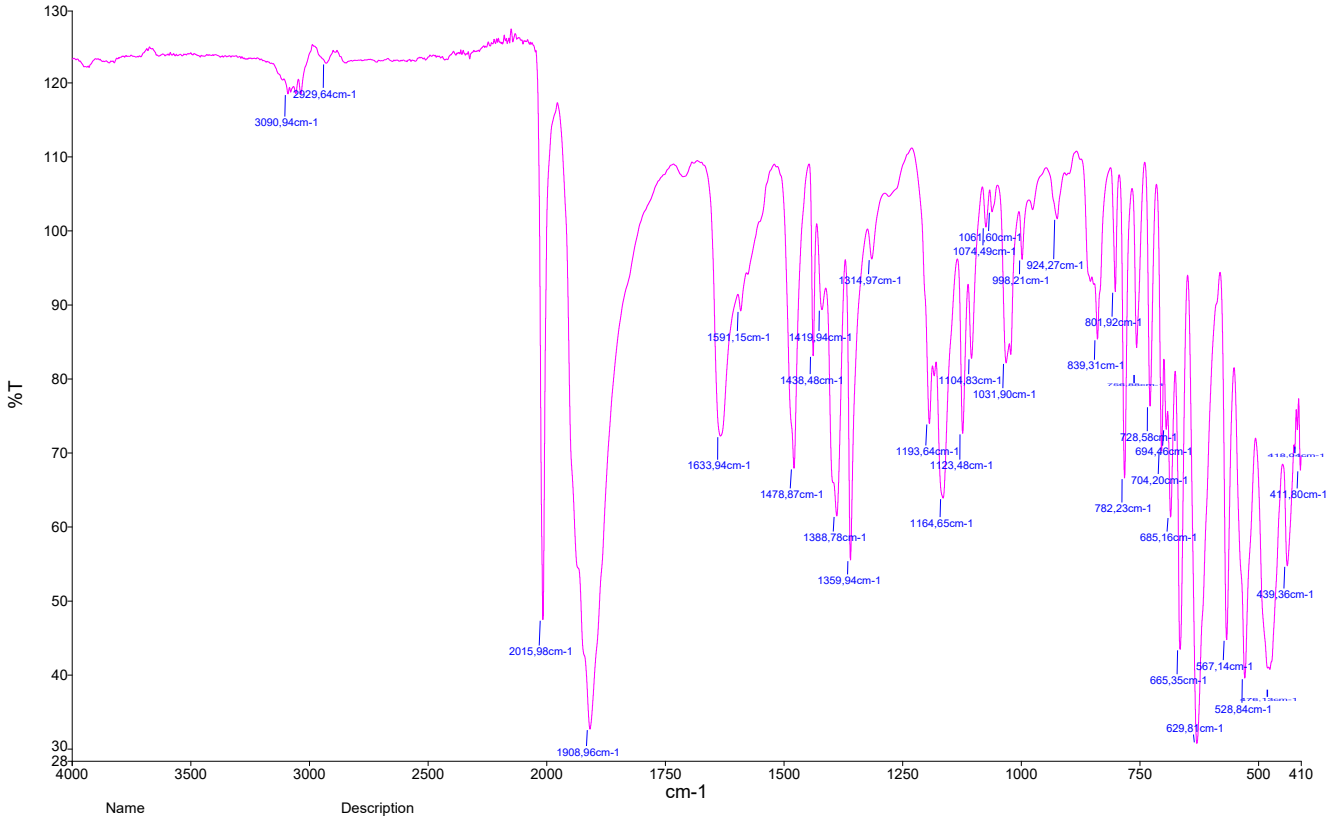

Figure S7. IR spectra of **2**.

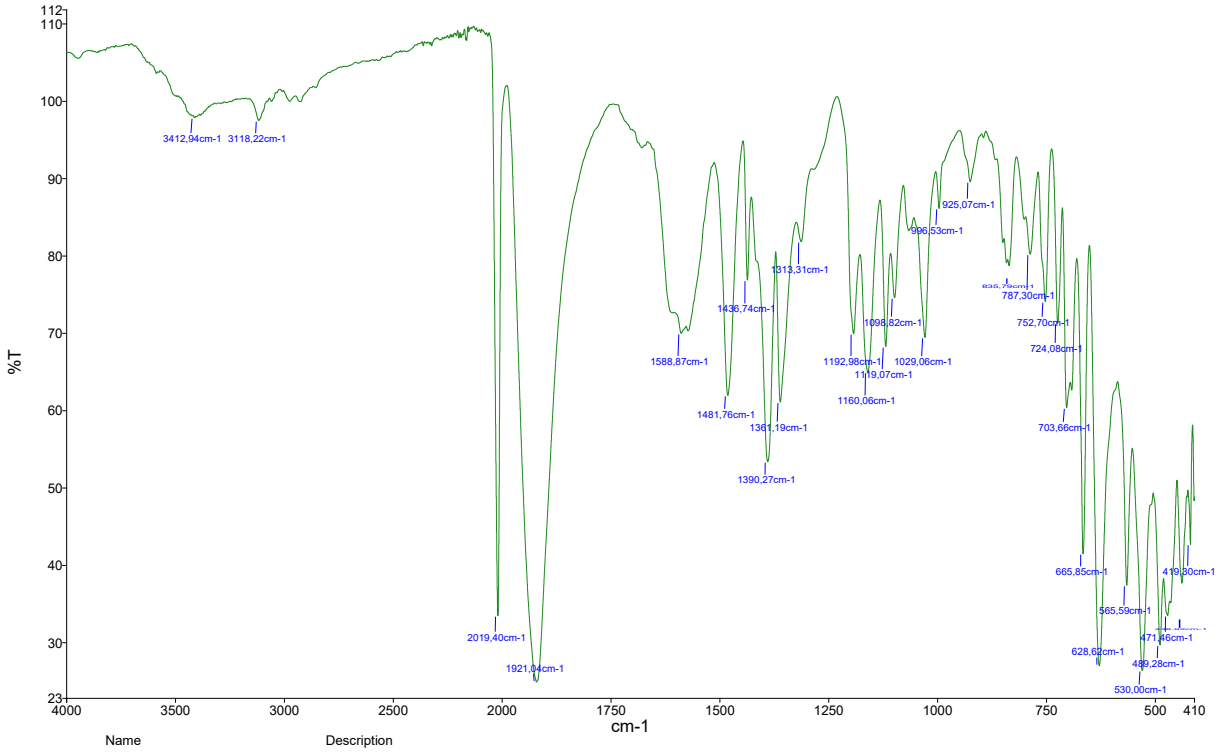

Figure S8. IR spectra of **3**.

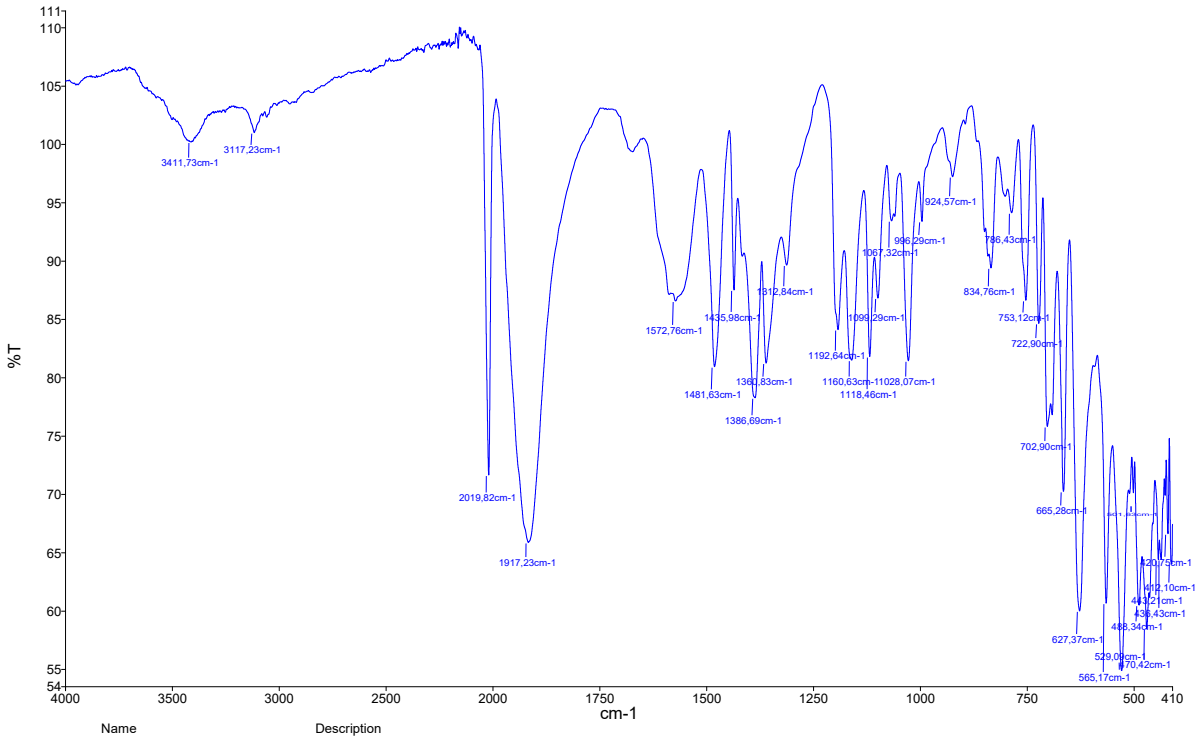

Figure S9. IR spectra of **4**.

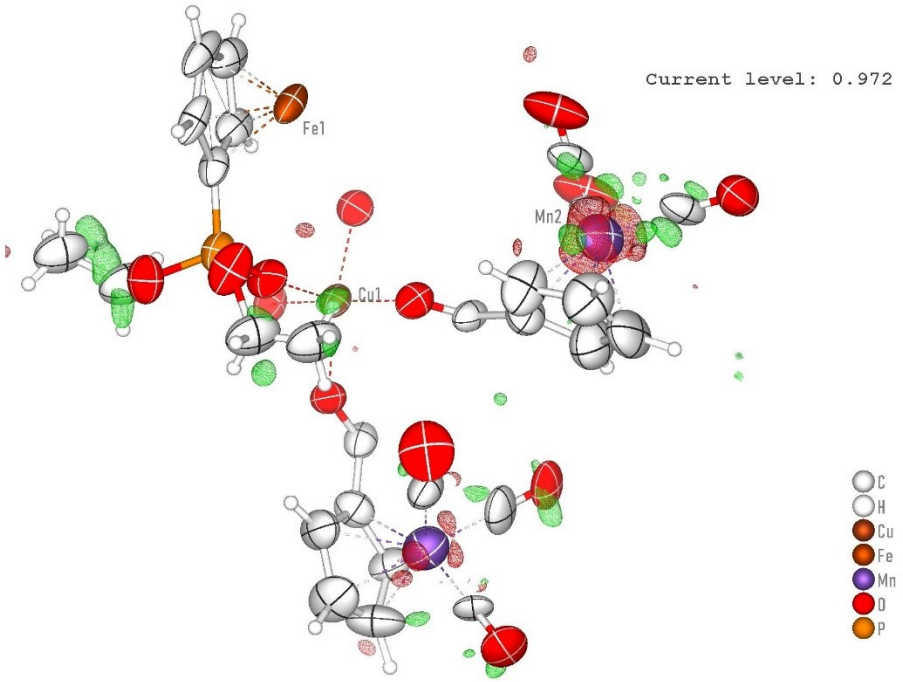

Figure S10. The residual electron density distribution in structure of **2.**

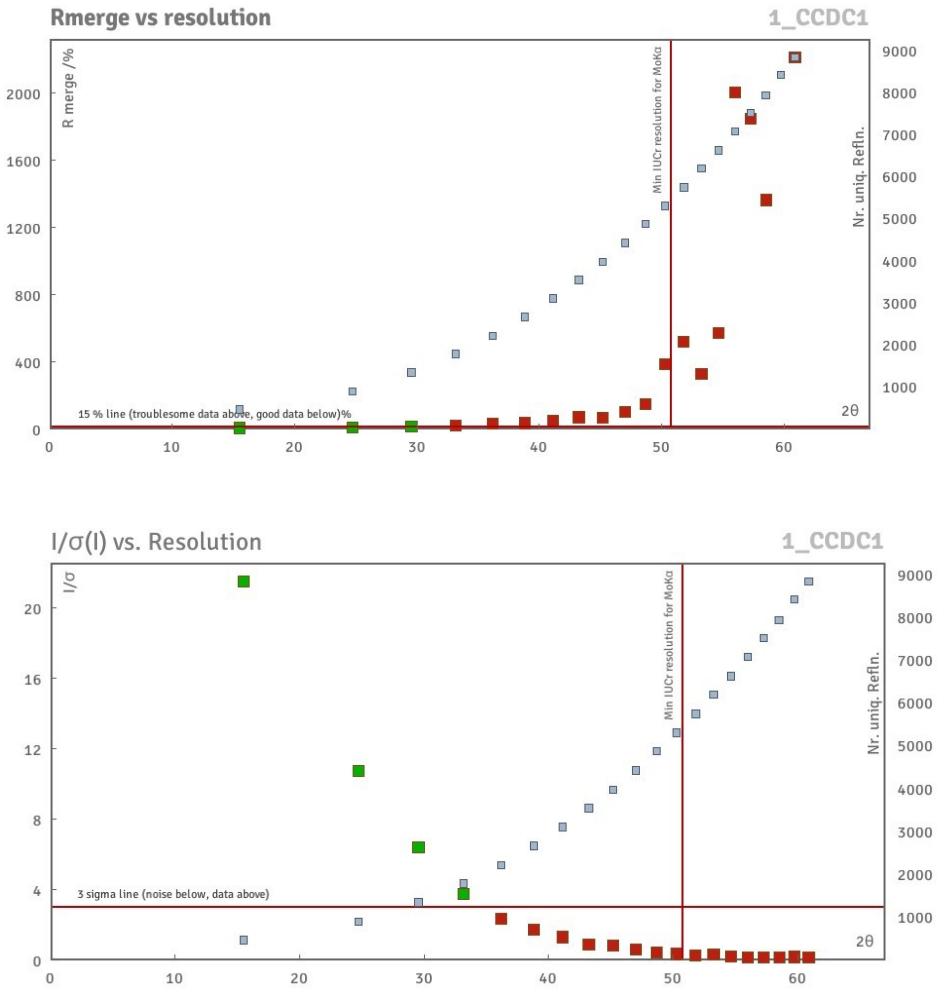

Figure S11. R merge_vs_resolution and I/σ(I)_vs_resolution for **2.** As an experiment, it was bad because the crystal was bad. But unfortunately, it is impossible to repeat this experiment for technical reasons (the starting materials are not available)

References

[1] SMART (control) and SAINT (integration) Software. Version 5.0. Madison (WI, USA): Bruker AXS Inc., **1997**.

[2] Sheldrick G.M. SADABS. Program for Scaling and Correction of Area Detector Data. Göttingen (Germany): Univ. of Göttingen, 1997.

[3] Dolomanov O. V., Bourhis L. J., Gildea R. J, Howard J. A. K., Puschmann H., J. Appl. Crystallogr., 2009, 42, 339–341.

[4] Sheldrick G.M., Acta Crystallogr. C, 2015, 71, 3-8.